The Significance of Photoelectric Technology in the Study of Ceramics Unearthed from the Zhouqiao Site in Kaifeng, Henan Province

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Abstract: This article firstly introduces recent dilemmas of traditional archaeological methods in archaeological studies. To solve these problems, bringing in modern scientific technologies is necessary. Then explaining working principles of photoelectric technology equipment like TEM, SEM, XRF, XPS, and their applications in field of archaeology. Finally in a case study of unearthed ceramics from Zhouqiao site in Kaifeng, listing some practical academic problems can be solved by above technologies.

Keywords: Photoelectric Technology; Zhouqiao Site in Kaifeng; Ceramic Archaeology; Archaeological Science

1. Dilemmas of traditional archaeological methods in ceramic research

Archeology is a discipline that recovers history by studying remains left by human beings. Modern archaeology came into being in Europe in the first half of the 19th century. During early 20th century, archeology was introduced to China, already 100 years until now. In the discipline of archaeology, field archaeology which mainly includes two major steps is the main course of archaeology. Two major steps are field excavation and indoor study, which respectively correspond to the two basic methods, stratigraphy and typology. Stratigraphy is mainly used in archaeological excavations, where excavators distinguish strata by identifying soil texture and color. According to principles of stratigraphy, the strata are stacked in sequence, time of the lower layer is earlier than that of the upper layer, so are the remains contained in the stratigraphy. After the excavators move remains indoor, using typology to classify and date those wares is crucial. By sorting out all remains, the excavators can summarize the type changes of wares over time.

From above opinion, traditional archaeological methods are still fundamental. However, if we only rely on the traditional, much information about remains will not be fully obtained. Taking the study of ceramics as an example, traditional methods mainly rely on personal experience of excavators to analyze found ceramics. Such experience can be indeed mostly effective, such as matching ceramic shards from city to those of kilns based on some characteristics of body and glaze of a ware, dating time based on shape, decoration and so on. However, in recent years, much those experience have proved to be inaccurate. For example, in tradition, high-quality Qingbai ware of Song Dynasty comes from the Hutian kiln in Jingdezhen, while poor-quality one belongs to other Jingdezhen kilns or similar kilns outside Jingdezhen. In fact, they are indistinguishable with naked eyes; transmutation glazed ware during the Jin and Yuan Dynasties in northern China are collectively called Jun kiln or Jun ware. By the Yuan Dynasty, transmutation glazed technology had spread from Junzhou Henan province to many kilns in different places. How to differentiate similar transmutation glazed from various kilns is another challenge for traditional archaeology.

History requires both macroscopic overview and microscopic observation. Although traditional ceramic archaeology has successfully constructed a frame for history through stratigraphy and typology, it neglects ceramics themselves, especially in microscopic study of artifacts. Microscopic research is to know some certain characteristics of objects that are beyond range of human perception such as firing temperature of ceramics, water absorption, composition of glaze elements and so on. Identifying these characteristics through scientific means can further understand our ancestors' craftsmanship and thinking in making ceramics, which will greatly deepen and widen archaeological research.

2. Principles and application of photoelectric equipment in ceramic archeology

Photoelectronic technology is a subject that studies the conversion between light and electricity. The operation of photoelectric equipment is mainly based on the photoelectric effect around sample. There are many types of photoelectric effects, including photoelectron emission effect, photoelectron induction effect, photovoltaic effect, etc. Simply to say, it is the phenomenon that the electronic system in a solid directly absorbs light energy, thereby changing the electrical properties of the solid. Different solids have different structures inside, and different reactions to light absorption and electron reflection. Because of its high sensitivity and low inertness, photoelectric instruments can widely detect radiation of different wave, which plays an important role in accurately detecting the elemental composition, microstructure and other physical and chemical characteristics of silicate ceramic products. The following introduces two types of photoelectric instruments that are commonly used in ceramic archeology.

2.1 Electron microscope

An electron microscope is a instrument based on the principle of electron optics, which uses electron beams, lenses and electromagnetic deflection, scattering electron generated by the interaction between electrons and solid so that structure of solid can be known. Interaction between electrons and solid will produce transmitted electrons, elastically scattered electrons, energy loss electrons, secondary electrons, X-rays, absorption electrons, etc. Electron microscope observe those electrons to check composition and structure of a sample. There are two main types of electron microscope often used in ceramic research.

Transmission electron microscope (TEM). Its principle is projecting an accelerated and concentrated transmission electron beam onto a very thin sample, thickness of which is usually less than 150nm. Electrons collide with atoms in a sample and change its direction, resulting in multi-angle scattering. Size of the scattering angle is related to the density and thickness of sample. In the process of scattering, a 2D projection image can be formed. After the image is enlarged and focused, it can be directly imaged on a CCD fluorescent screen or PC screen. The transmission electron microscope has a magnification of more than 50 million, but field angle is limited and the resolution is less than 50pm.

Here are two examples of the application of TEM in ceramic research. The first is a research on ancient Roman red pottery (terra sigillata) by researcher Pilippe Sciau of the French National Center for Scientific Research (CEMES-CNRS). The experiment used TEM to analyze the red pottery produced in the South Gaul region. The pottery coating is mainly composed of glass containing hematite crystals and smaller corundum crystals. The corundum content in the pottery is high and the magnesium content is low, while Italian pottery made in Earlier Roman time contained more magnesium-aluminum spinel and higher magnesium content. This analysis effectively distinguishes the ancient Roman red potteries that look very similar between Southern Gaul and Italy so it is significant to ancient Roman pottery studies(according to Pilippe Sciau's lecture in Chinese Academy of Social Sciences, 2019). Another successful case is that a team from Peking University used FIB-TEM, to analyze the residual color particles in sub-micron from the blue and white porcelain of the Xuande imperial kiln of Ming dynasty in Jingdezhen. The mixed use of domestic and imported cobalt materials in blue and white porcelain reveals a global industrial chain in Jingdezhen during 14th and 15th centuries.

Scanning electron microscope (SEM). It is similar to TEM. The difference is that the SEM is scattering electrons with a large field angle, but magnification is only 1-2 million, and resolution is about 3-6nm, can form a 3D image of the sample surface. The image needs to be captured and counted by the detector before it can be displayed on PC screen. SEM is easy to make samples which can be observed by coating the surface with a conductive layer. Therefore, in practice of ceramic research, SEM is more popular than TEM. An case of using SEM to analyze ceramics to solve related archaeological issues includes a study of local iron workshops in Western Han Dynasty by scholars Lin Yongchang of the Chinese University of Hong Kong. The researcher used petrography and SEM to analyze the iron-smelting-related potteries unearthed from the workshop in Shaanxi, such as pottery molds, blast pipes, and furnace walls. They concluded that these potteries had been specialized made respectively, indicating that this small workshop had a complex division and highly specialized production at that time.

2.2 X-ray Fluorescence (XRF) and X-ray Photoelectron Spectroscopy (XPS)

XRF uses X-rays to activate electrons in sample's inner layer, and detects the corresponding elements by measuring the rays emitted by different elements. There are different types of XRF, one of which is Energy Dispersive X-ray Fluorescence (EDXRF). EDXRF is most widely used in the ceramic because of its semiconductor detectors with good energy resolution. And other merits of XRF are like conducting non-destructive testing of samples, high speed analysis, simple processing, easy interpretation of spectra and so on. Since 21st century, portable XRF equipment has gradually been matured so it has become the most frequently used composition analysis instrument in field archaeology. Applied case of EDXRF is a study carried out by Shaanxi University of Science and Technology and Shanxi Provincial Institute of Archeology. This study used EDXRF and spectrophotometer to conduct chemical composition and glaze color analysis of 135 ceramic samples from different kiln sites in southern Shanxi, revealing characteristics of ceramics in southern Shanxi like differences in raw material sources and craftsmanship among kiln sites. Institute of Guangxi Archaeological also used EDXRF to analyze the glaze composition of 24 excavated pieces of copper-glazed ceramics from the Yongfu Kiln of the Song Dynasty. Result shows that the formation of glaze colors such as copper red, emerald green, and dark green should be related to factors such as copper content in the glaze or firing atmosphere. This research suggests that the green glazed ware is main product in Yongfu Kiln, the copper-red and other glazed colors should be accidentally made inside kiln furnace.

XPS can effectively obtain the chemical elements from ceramic body and glaze, especially in analysis of some metal elements such as iron, copper, cobalt. Also it is be able to figure out its firing temperature, glaze color mechanism and so on. XPS has some merit like high sensitivity, time saving, small sample consumption, even low damage to the sample. However, in order to make the results of analysis accurate, XPS often cooperates with XRF, XRD. A important case is a study of the discoloration mechanism of yellow and green glazed tiles unearthed from the Yuanmingyuan site in Beijing by the University of Chinese Academy of Sciences, Peking University and the Beijing Institute of Cultural Relics. The experiment shows that the iron elements of yellow glazed tiles are Fe^{3+} and Fe^{2+}. Under high temperature conditions, Fe^{2+} is oxidized to Fe^{3+}, and Fe^{3+} is precipitated and became into hexagonal flake-shaped crystal particles of α-Fe_2O_3, causing glazed tile to appear red. Copper in green glazed tiles exists in the form of Cu^{2+}, which is reduced to CuO and Cu_2O under high temperature conditions, thus appearing bright red or black red.

3. The archaeological value of introducing photoelectric technology into the study of ceramics unearthed from Zhouqiao site in Kaifeng

As one of the eight ancient capitals of China, Kaifeng had created a splendid urban civilization. Located on the central axis of Kaifeng city, the location of Zhouqiao site has been acting as city center for more than a thousand years. Zhouqiao bridge was first built in the Jianzhong period of the Tang Dynasty, and was completely buried by the silt after the Yellow River flooded in 1642, at the end of the Ming Dynasty. Since 2018, the Henan Provincial Institute of Cultural Relics and Archeology have conducted academic archaeological excavations at the site, revealing a large number of relics and remains. Among them, the number of ceramics is the largest. Time of tens of thousands of ceramics span from Song to Qing Dynasty and origin kilns of them are also widely spread. Conducting research on these unearthed ceramics in Kaifeng has two main meanings: Firstly, we can know the development of the commodity economy of Kaifeng City through ceramics which were important trade commodities. Secondly, ceramics can comprehensively reflect the production situation of China's ancient ceramic-making industry. Exploring the process of making ceramics is to recover a living history of ancient science and technology. However, as it mentioned above, traditional archaeological study on ceramics has limits. The introduction of photoelectric technology, such as TEM, SEM, XRF, XPS will be helpful to solve archaeological problems at Zhouqiao site.

3.1 Distinguishing kiln origins among similar types of ceramics

Regarding research on the origin of ceramics, it has been roughly proved by using typology to classify unearthed shards. For example, the Qingbai wares of the Northern Song Dynasty basically came from the Jingdezhen kiln, and celadon with printed patterns came from the Yaozhou in Shaanxi province or Linru kiln in Henan province, the high-quality celadon of Song and Jin Dynasties came from the central and western regions of Henan, most Jun wares came from Henan, blue and white porcelain of Yuan, Ming and Qing Dynasties basically came from Jingdezhen kiln, white glazed wares with slip mainly came from the north of China. However, with qualitative analysis of typology is not precisely enough. First of all, Qingbai ware during the Northern Song Dynasty were not only produced in Jingdezhen, but also in Fanchang of Anhui province, Baishe Kiln in Jiangxi province or other areas by Yangtze River. Firing techniques of these kilns are closely related to the Jingdezhen kilns, so the level of quality can only represent the majority, not all, the ones with poor quality might be produced in Jingdezhen, with good quality might be from other kilns. Mistakes by quality standards are often taken to distinguish Yaozhou with Linru celadon and blue and white porcelain in Jingdezhen with Fujian or Zhejiang province. Secondly, it is not appropriate to use economic principles as a standard for determining kiln production. When researchers face similar wares from two or more kilns, they tend to attribute production origin to closest kilns near consuming area. For example, white glazed wares with slip unearthed in Kaifeng are more likely to come from Yuzhou kilns in Henan province rather than the further Cizhou kilns. That economic principle has ignored the complexity of ancient trade and transportation. Thirdly, if the previous two principles cannot solve the problem, traditional scholars will not be able to determine the kiln origin, then use a concept named Kiln System instead. For example, the Jun-glazed ware of the Jin and Yuan Dynasties unearthed in Kaifeng is collectively called the Jun Kiln System.

Those problems can be well solved with the support of XRF technology. Ancient Chinese ceramics were basically made from local materials. The mineral resources involved in the body and glaze are generally near the kiln site, and have different elements. XRF uses photoelectric technology to obtain the constituent elements of wares in consuming and producing places, then compares the composition of these elements. Ultimately, origin area of wares can be narrowed down and pinned. Also some unknown kilns could be found by using this technology to detect mineral products around known kilns.

3.2 Study on craftsmanship of various ceramics

A large number of ceramic shards from various periods and origins across the country have been unearthed at the Zhouqiao site, which is very convenient for observing and comparing ceramic making craftsmanship. Recovering craftsmanship of ancient ceramics is one of the difficult problems in ceramic archeology. Taking the distinction between the slip and the middle layer under glaze as an example, Henan celadon and Jun-glazed wares from the Song, Jin and Yuan Dynasties from Zhouqiao generally have a white layer between the body and glaze. This white layer seems similar to slip whose main function is to make glaze whiter, but applying it on opaque Jun ware seems unnecessary. So there are two problems needs to be solved. Firstly, If this layer of Henan celadon is to imitate Yaozhou celadon of the Fifth Dynasty, making glaze look brighter and more beautiful, then whether this layer has the same ingredients as slip; if not as man-made slip, but a reflection layer between glaze and body, was it formed naturally at the beginning but controlled by ancient workers later so that the specific formula could lead to same decorative effect as slip?

It cannot be answered simply by observing this layer with naked eyes or an optical microscope. Through TEM or SEM technology, middle layer can be effectively magnified to a million times, or even tens of millions of times so that the microstructure of layer can be clearly seen. Different materials have different microstructure. Based on this principle, what kind of microstructure this layer belongs to can be further determined. To improve the accuracy of experiments, TEM or SEM technology can also be applied with XRF or XPS technology. Based on combined composition analysis, we can know what kind of formula this layer could be and by comparing with same technology where a formula came from. Those assumption are keys to bridging between archaeological remains and live human history.

4. Conclusion

Scientific archaeology is an inevitable trend in the development of discipline. Gradually there are many scientific methods used in the field of archaeology, and in ceramic archaeology, photoelectric technology is undoubtedly the most popular, especially electron microscope and X-ray electron fluorescence technology. They can safely and effectively let archaeologists go into a microscopic world of ceramics, obtain deep information such as the elemental composition and existing status of ceramics. It lay a solid foundation for recovering history. By now, photoelectronic technology equipment mentioned above still have various problems in practical, for example, high cost of equipment leads to low popularizing rate; some instruments have irreversible damage to artefacts; errors in same test samples under different environments; practitioners lack sufficient professional knowledge and result in equipment damage. With the development and closer cooperation of science and technology, shortcomings will be gradually revised and improved in the future.

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